(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
20 November 2003 (20.11.2003)

PCT

(10) International Publication Number
WO 03/095702 A2

(51) International Patent Classification[7]: C23C 16/30

(21) International Application Number: PCT/US03/14272

(22) International Filing Date: 8 May 2003 (08.05.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

60/378,799	8 May 2002 (08.05.2002)	US
10/302,375	22 November 2002 (22.11.2002)	US
10/302,393	22 November 2002 (22.11.2002)	US
10/409,887	8 April 2003 (08.04.2003)	US

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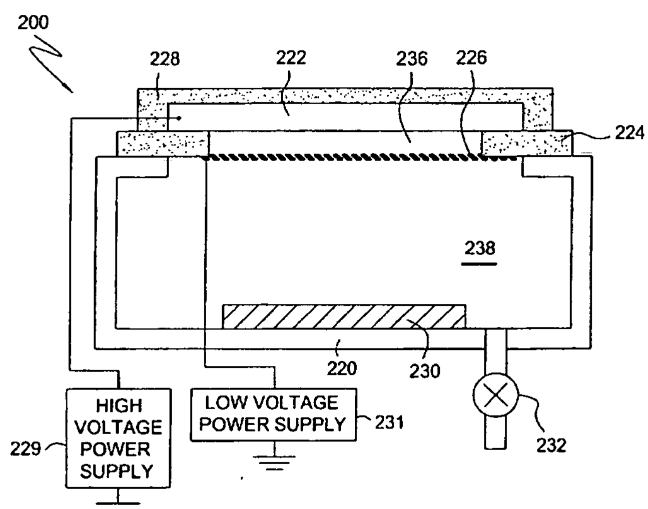
(54) Title: METHOD FOR CURING LOW DIELECTRIC CONSTANT FILM BY ELECTRON BEAM



WO 03/095702 A2

(57) Abstract: A method for depositing a low dielectric constant film on a substrate. The method includes depositing a low dielectric constant film comprising silicon, carbon, oxygen and hydrogen in a chemical vapor deposition chamber. The method further includes exposing the low dielectric constant film to an electron beam at conditions sufficient to increase the hardness of the low dielectric constant film.

(81) **Designated States** *(national)*: CN, JP, KR, SG.

(84) **Designated States** *(regional)*: European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR).

Published:
— *without international search report and to be republished upon receipt of that report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

METHOD FOR CURING LOW DIELECTRIC CONSTANT FILM BY ELECTRON BEAM

BACKGROUND OF THE INVENTION

[0001] **Field of the Invention**

[0002] Embodiments of the present invention relate to the fabrication of integrated circuits. More particularly, embodiments of the present invention relate to a process for depositing dielectric layers on a substrate.

[0003] **Description of the Related Art**

[0004] Integrated circuit geometries have dramatically decreased in size since such devices were first introduced several decades ago. Since then, integrated circuits have generally followed the two year/half-size rule (often called Moore's Law), which means that the number of devices on a chip doubles every two years. Today's fabrication facilities are routinely producing devices having 0.13 μm and even 0.1 μm feature sizes, and tomorrow's facilities soon will be producing devices having even smaller feature sizes.

[0005] The continued reduction in device geometries has generated a demand for films having lower k values because the capacitive coupling between adjacent metal lines must be reduced to further reduce the size of devices on integrated circuits. In particular, insulators having low dielectric constants (k), less than about 4.0, are desirable. Examples of insulators having low dielectric constants include spin-on glass, un-doped silicon glass (USG), fluorine-doped silicon glass (FSG), and polytetrafluoroethylene (PTFE), which are all commercially available.

[0006] An effective method to reduce the k value is to introduce pores into the film. As a result, low k films often have a low mechanical strength (e.g., hardness), which may hinder the integration of the films into the manufacture of the device. Plasma post treatment is currently being used to increase the mechanical strength of low k films. However, the plasma treatment causes the k value to increase.

[0007] A need, therefore, exists for a method to increase the mechanical strength of low k films without increasing the k value.

SUMMARY OF THE INVENTION

[0008] Embodiments of the present invention are generally directed to a method for depositing a low dielectric constant film on a substrate. The method includes depositing a low dielectric constant film comprising silicon, carbon, oxygen and hydrogen in a chemical vapor deposition chamber. The method further includes exposing the low dielectric constant film to an electron beam at conditions sufficient to increase the hardness of the low dielectric constant film.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] So that the manner in which the above recited features of the present invention can be understood in detail, a more particular description of the invention, briefly summarized above, may be had by reference to embodiments, some of which are illustrated in the appended drawings. It is to be noted, however, that the appended drawings illustrate only typical embodiments of this invention and are therefore not to be considered limiting of its scope, for the invention may admit to other equally effective embodiments.

[0010] Figure 1 is a cross-sectional diagram of an exemplary CVD reactor configured for use according to embodiments described herein.

[0011] Figure 2 is an electron beam chamber in accordance with an embodiment of the invention.

[0012] Figure 3 is a fragmentary view of the electron beam chamber in accordance with an embodiment of the invention.

[0013] Figure 4 illustrates the electron beam chamber with a feedback control circuit in accordance with an embodiment of the invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

[0014] A detailed description will now be provided. Various terms as used herein are defined below. To the extent a term used in a claim is not defined below, it should be given the broadest definition persons in the pertinent art have given that term, as reflected in printed publications and issued patents. Embodiments of the invention provide a significant and unexpected improvement in hardness, cracking threshold and electrical properties (e.g., leakage current and break down voltage) of

an ultra low dielectric constant film. In one embodiment, a film containing silicon, carbon, oxygen, and hydrogen is deposited on a surface of a substrate at conditions sufficient to form an ultra low dielectric constant film (k less than 2.5). The ultra low dielectric constant film is then subjected to a post treatment of electron beam.

[0015] In accordance with one or more embodiments of the present invention, one or more film properties such as, for example, and without limitation, mechanical properties, thermal stability, dielectric constant, etch selectivity, resistance to isotropic strip processes (for example, a non-cross-linked polymer may etch easily with an isotropic down-stream plasma strip process), and copper diffusion barrier characteristics are improved by electron-beam ("e-beam") treatment. It is believed that, at least in one respect, e-beam treatment provides such improvement because the e-beam treatment acts to dehydrogenatively cross-link the film (i.e., it is believed that the e-beam treatment acts preferentially to remove hydrogen bonds, thereby enabling cross-linking of carbon bonds), thereby densifying and increasing the surface hardness and the Young's modulus of the film. It is further believed that at least in most cases this is accomplished without substantially changing its bulk composition.

[0016] In accordance with one or more embodiments of the present invention, in a first step of a method of producing a low-k dielectric film, a lower-k dielectric film is deposited using a CVD deposition process (in the manner described in detail below), which lower-k dielectric film may contain a predetermined porosity. Normally, such a CVD-deposited film would be soft, and contain metastable species. When such a CVD-deposited film is thermally annealed, metastable species are driven off, and the film shrinks --such a film might have a k value of ~2.6. A plasma anneal process has been used to reduce the time it takes to carry out a thermal anneal by exposing the film to a plasma environment. However, the plasma anneal process is ineffective because its effect is limited to the surface of the film. Next, in accordance with this embodiment of the present invention, in a second step of the method of producing a low-k dielectric film, an e-beam treatment (including heating the film at the same time) is carried out on the CVD-deposited film to convert it into a hard, heavily cross-linked film. Finally, in accordance with this embodiment of the present invention, in an optional third step of the method of

producing a low-k dielectric film, the e-beam treated film may be thermally annealed. Advantageously, e-beam treating the CVD-deposited film strengthens the structure of the film while driving out metastable species to prevent shrinking.

[0017] One embodiment of a method for depositing a lower dielectric constant film containing silicon, oxygen, and carbon entails the use of a precursor comprised of one or more cyclic organo-silicon-based compounds. Further such embodiments entail blending one or more cyclic organo-silicon-based compounds and one or more acyclic organo-silicon compounds. In one aspect, a cyclic organo-silicon compound, an acyclic organo-silicon, and a hydrocarbon compound are reacted with an oxidizing gas at conditions sufficient to form a low dielectric constant film having k less than 2.5. The cyclic organo-silicon compound includes at least one silicon-carbon bond. The acyclic organo-silicon compound includes, for example, and without limitation, a silicon-hydrogen bond or a silicon-oxygen bond. The hydrocarbon could be linear or cyclic, and may include a carbon-carbon double or triple bond. In accordance with one or more embodiments of the present invention, if at least one the organo-silicon gases contains oxygen, one may not need an oxidizing gas.

[0018] The CVD films contain a network of -Si-O-Si- ring structures that are cross-linked with one or more linear organic compounds. Because of the cross-linkage, a reactively stable network is produced having a greater separation between ring structures and thus, the deposited films possess a greater degree of porosity.

[0019] The ultra low dielectric constant film is generally formed by blending or mixing one or more precursor gases, which may include cyclic organosilicon compounds, aliphatic compounds, hydrocarbon compounds, and oxidizing compounds. The cyclic organosilicon compounds may include a ring structure having three or more silicon atoms and the ring structure may further comprise one or more oxygen atoms. Commercially available cyclic organosilicon compounds include rings having alternating silicon and oxygen atoms with one or two alkyl groups bonded to the silicon atoms. For example, the cyclic organosilicon compounds may include one or more of the following compounds:

1,3,5-trisilano-2,4,6-trimethylene,	$(-SiH_2-CH_2-)_3-$ (cyclic)
1,3,5,7-tetramethylcyclotetrasiloxane (TMCTS),	$(-SiH(CH_3)-O-)_4-$ (cyclic)
octamethylcyclotetrasiloxane (OMCTS),	$(-Si(CH_3)_2-O-)_4-$ (cyclic)
1,3,5,7,9-pentamethylcyclopentasiloxane,	$(-SiH(CH_3)-O-)_5-$ (cyclic)
1,3,5,7-tetrasilano-2,6-dioxy-4,8-dimethylene,	$(-SiH_2-CH_2-SiH_2-O-)_2-$ (cyclic)
hexamethylcyclotrisiloxane	$(-Si(CH_3)_2-O-)_3-$ (cyclic)

[0020] The aliphatic compounds include linear or branched (i.e. acyclic) organosilicon compounds having one or more silicon atoms, one or more carbon atoms, and linear or branched hydrocarbon compounds having at least one unsaturated carbon bond. The structures may further comprise oxygen. Commercially available aliphatic organosilicon compounds include organosilanes that do not contain oxygen between silicon atoms and organosiloxanes that contain oxygen between two or more silicon atoms. For example, the aliphatic organosilicon compounds may include one or more of the following compounds:

methylsilane	CH_3-SiH_3
dimethylsilane	$(CH3)_2-SiH_2$
trimethylsilane	$(CH3)_3-SiH$
diethoxymethylsilane (DEMS),	$CH_3-SiH-(O-CH_2-CH_3)_2$
dimethyldimethoxysilane (DMDMOS)	$(CH_3O)_2-Si-(CH_3)_2$
dimethyldimethoxysilane	$(CH3)_2-Si-(O-CH_3)_2$
ethylsilane	$CH_3-CH_2-SiH_3$
disilanomethane	$SiH_3-CH_2-SiH_3$
bis(methylsilano)methane	$CH_3-SiH_2-CH_2-SiH_2-CH_3$
1,2-disilanoethane	$SiH_3-CH_2-CH_2-SiH_3$
1,2-bis(methylsilano)ethane	$CH_3-SiH_2-CH_2-CH_2-SiH_2-CH_3$
2,2-disilanopropane	$SiH_3-C(CH_3)_2-SiH_3$
1,3-dimethyldisiloxane	$CH_3-SiH_2-O-SiH_2-CH_3$
1,1,3,3-tetramethyldisiloxane (TMDSO)	$(CH_3)_2-SiH-O-SiH-(CH_3)_2$
hexamethyldisiloxane (HMDS)	$(CH_3)_3-Si-O-Si-(CH_3)_3$
1,3-bis(silanomethylene)disiloxane	$(SiH_3-CH_2-SiH_2-)_2-O$
bis(1-methyldisiloxanyl)methane	$(CH_3-SiH_2-O-SiH_2-)_2-CH_2$
2,2-bis(1-methyldisiloxanyl)propane	$(CH_3-SiH_2-O-SiH_2-)_2-C(CH_3)_2$
hexamethoxydisiloxane (HMDOS)	$(CH_3-O)_3-Si-O-Si-(O-CH_3)_3$
diethylsilane	$(C_2H_5)_2SiH_2$
propylsilane	$C_3H_7SiH_3$
vinylmethylsilane	$CH_2=CH-SiH_2-CH_3$
1,1,2,2-tetramethyldisilane	$(CH_3)_2-SiH-SiH-(CH_3)_2$

hexamethyldisilane	$(CH_3)_3$-Si—Si-$(CH_3)_3$
1,1,2,2,3,3-hexamethyltrisilane	$(CH_3)_2$-SiH—Si$(CH_3)_2$—SiH-$(CH_3)_2$
1,1,2,3,3-pentamethyltrisilane	$(CH_3)_2$SiH—SiH(CH_3)—SiH$(CH_3)_2$
dimethyldisilanoethane	CH_3-SiH_2-$(CH_2)_2$-SiH_2-CH_3
dimethyldisilanopropane	CH_3-SiH-$(CH_2)_3$-SiH-CH_3
tetramethyldisilanoethane	$(CH_3)_2$-SiH-$(CH_2)_2$-SiH-$(CH_3)_2$
tetramethyldisilanopropane	$(CH_3)_2$-SiH-$(CH_2)_3$-Si-$(CH_3)_2$

[0021] The hydrocarbon compounds have between one and about 20 adjacent carbon atoms. The hydrocarbon compounds may include adjacent carbon atoms that are bonded by any combination of single, double, and triple bonds. For example, the organic compounds may include alkenes and alkylenes having two to about 20 carbon atoms, such as ethylene, propylene, acetylene, butadiene, t-butylethylene, 1,1,3,3-tetramethylbutylbenzene, t-butylether, methyl-methacrylate (MMA), and t-butylfurfurylether.

[0022] The organosilicon compounds further include organosilicon compounds having a hydrocarbon component having one or more unsaturated carbon-carbon bonds, such as carbon-carbon double bonds, carbon-carbon triple bonds, or aromatic groups. For example, the organosilicon compounds having a hydrocarbon component having one or more unsaturated carbon-carbon bonds may include one or more of the following compounds:

vinylmethylsilane	CH_2=$CHSiH_2CH_3$,
dimethoxymethylvinylsilane (DMMVS)	$(CH_3O)_2$-Si(CH_3)-CH=CH_2,
trimethylsilylacetylene	$(CH_3)_3$Si-C≡CH,
1-(trimethylsilyl)-1,3-butadiene	$(CH_3)_3$Si-HC≡CH-HC≡CH_2,
trimethylsilylcyclopentadiene	$(CH_3)_3$Si-C_5H_5,
trimethylsilylacetate	$(CH_3)_3$Si-O(C=O)CH_3,
di-tertbutoxydiacetoxysilane	$((CH_3)_3(C$=$O))_2$-Si-$((C$=$O)(CH_3)_3)_2$.

[0023] In one embodiment, one or more organosilicon compounds having a hydrocarbon component having one or more unsaturated carbon-carbon bonds is reacted with one or more oxidizing gases and delivered to a substrate surface at conditions sufficient to deposit a low dielectric constant film on the substrate.

[0024] In another embodiment, one or more organosilicon compounds and one or more aliphatic hydrocarbons are reacted with one or more oxidizing gases and delivered to a substrate surface at conditions sufficient to deposit a low dielectric constant film on the substrate. The aliphatic hydrocarbon compounds may include between one and about 20 adjacent carbon atoms. The hydrocarbon compounds can include adjacent carbon atoms that are bonded by any combination of single, double, and triple bonds. Preferably, the aliphatic hydrocarbon compounds include at least one unsaturated carbon-carbon bond. For example, the aliphatic compounds may include alkenes, alkylenes, and dienes having two to about 20 carbon atoms, such as ethylene, propylene, isobutylene, acetylene, allylene, ethylacetylene, 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, and piperylene.

[0025] In another embodiment, the present invention includes a significant and unexpected reduction in dielectric constants for films comprising silicon, oxygen, and carbon by blending one or more compounds having at least one cyclic group, one or more organosilicon compounds, and optionally an oxidizing gas at conditions sufficient to form a pre-treated film network. In one aspect, one or more organic compounds having at least one cyclic group and one or more organosilicon compounds are reacted with an oxidizing gas in amounts sufficient to deposit a low dielectric constant film on a semiconductor substrate.

[0026] The film may be deposited using plasma assistance within a processing chamber capable of performing chemical vapor deposition (CVD). The plasma may be generated using pulse RF, high frequency RF, dual frequency, dual phase RF, or any other known or yet to be discovered plasma generation technique. Following deposition of the film, the film is cured by electron beam to remove pendant organic groups, such as cyclic groups of the organic compounds that have been incorporated into the film network during deposition.

[0027] The curing step supplies energy to the film network to volatize and remove at least a portion of the cyclic groups in the film network, leaving behind a more porous film network having a lower dielectric constant. In most cases, the cured film demonstrates a hardness at least two times, and as much as 600%, more than a non-cured film deposited according to embodiments described herein. Films cured using e-beam show an unexpected reduction in k value and an unexpected

increase in hardness, not achievable with conventional curing techniques. Typically, the cured film has a dielectric constant of about 2.5 or less, preferably about 2.2 or less, and a hardness greater than about 0.6 GPa.

[0028] Regarding the one or more compounds having at least one cyclic group, "cyclic group" as used herein is intended to refer to a ring structure. The ring structure may contain as few as three atoms. The atoms may include carbon, silicon, nitrogen, oxygen, fluorine, and combinations thereof, for example. The cyclic group may include one or more single bonds, double bonds, triple bonds, and any combination thereof. For example, a cyclic group may include one or more aromatics, aryls, phenyls, cyclohexanes, cyclohexadienes, cycloheptadienes, and combinations thereof. The cyclic group may also be bi-cyclic or tri-cyclic. Further, the cyclic group is preferably bonded to a linear or branched functional group. The linear or branched functional group preferably contains an alkyl or vinyl alkyl group and has between one and twenty carbon atoms. The linear or branched functional group may also include oxygen atoms, such as a ketone, ether, and ester. Some exemplary compounds having at least one cyclic group include alpha-terpinene (ATP), vinylcyclohexane (VCH), and phenylacetate, just to name a few.

[0029] Some of the above-described precursors contain oxygen, therefore an additional oxidizer may not be needed. However, in any of the embodiments described herein, one or more oxidizing gases may be used. In case one or more oxidizing gases or liquids are needed, they may include oxygen (O_2), ozone (O_3), nitrous oxide (N_2O), carbon monoxide (CO), carbon dioxide (CO_2), water (H_2O), hydrogen peroxide (H_2O_2), an oxygen –containing organic compound, or combinations thereof. In one embodiment, the oxidizing gas is oxygen gas. In another embodiment, the oxidizing gas is ozone. When ozone is used as an oxidizing gas, an ozone generator converts from 6% to 20%, typically about 15%, by weight of the oxygen in a source gas to ozone, with the remainder typically being oxygen. However, the ozone concentration may be increased or decreased based upon the amount of ozone desired and the type of ozone- generating equipment used. The one or more oxidizing gases are added to the reactive gas mixture to increase reactivity and achieve the desired carbon content in the deposited film.

[0030] Deposition of the ultra low dielectric constant film can be continuous or discontinuous in a single deposition chamber. Alternatively, the film can be deposited sequentially in two or more deposition chambers, such as within a cluster tool like the Producer™ available from Applied Materials, Inc. of Santa Clara, California.

[0031] The deposited film contains a carbon content between about 5 and about 30 atomic percent (excluding hydrogen atoms), preferably between about 5 and about 20 atomic percent. The carbon content of the deposited films refers to atomic analysis of the film structure that typically does not contain significant amounts of non-bonded hydrocarbons. The carbon contents are represented by the percent of carbon atoms in the deposited film, excluding hydrogen atoms that are difficult to quantify. For example, a film having an average of one silicon atom, one oxygen atom, one carbon atom, and two hydrogen atoms has a carbon content of about 20 atomic percent (one carbon atom per five total atoms), or a carbon content of about 33 atomic percent, excluding hydrogen atoms (one carbon atom per three total atoms, other than hydrogen atoms).

[0032] The film may be deposited using any processing chamber capable of chemical vapor deposition (CVD). Referring now Figure 1, a vertical, cross-section view of a parallel plate CVD processing chamber 10 is illustrated. The chamber 10 includes a high vacuum region 15 and a gas distribution manifold 11 having perforated holes for dispersing process gases therethrough to a substrate (not shown). The substrate rests on a substrate support plate or susceptor 12. The susceptor 12 is mounted on a support stem 13 that connects the susceptor 12 to a lift motor 14. The lift motor 14 raises and lowers the susceptor 12 between a processing position and a lower, substrate-loading position so that the susceptor 12 (and the substrate supported on the upper surface of susceptor 12) can be controllably moved between a lower loading/off-loading position and an upper processing position which is closely adjacent to the manifold 11. An insulator 17 surrounds the susceptor 12 and the substrate when in an upper processing position.

[0033] Gases introduced to the manifold 11 are uniformly distributed radially across the surface of the substrate. A vacuum pump 32 having a throttle valve controls the exhaust rate of gases from the chamber 10 through a manifold 24.

Deposition and carrier gases, if needed, flow through gas lines 18 into a mixing system 19 and then to the manifold 11. Generally, each process gas supply line 18 includes (i) safety shut-off valves (not shown) that can be used to automatically or manually shut off the flow of process gas into the chamber, and (ii) mass flow controllers (also not shown) to measure the flow of gas through the gas supply lines 18. When toxic gases are used in the process, several safety shut-off valves are positioned on each gas supply line 18 in conventional configurations.

[0034] During deposition, a blend/mixture of one or more cyclic organosilicon compounds and one or more aliphatic compounds are reacted with an oxidizing gas to form an ultra low k film on the substrate. The cyclic organosilicon compounds may be combined with at least one aliphatic organosilicon compound and at least one aliphatic hydrocarbon compound. For example, the mixture contains about 5 percent by volume to about 80 percent by volume of the one or more cyclic organosilicon compounds, about 5 percent by volume to about 15 percent by volume of the one or more aliphatic organosilicon compounds, and about 5 percent by volume to about 45 percent by volume of the one or more aliphatic hydrocarbon compounds. The mixture also contains about 5 percent by volume to about 20 percent by volume of the one or more oxidizing gases. Alternatively, the mixture may contain about 45 percent by volume to about 60 percent by volume of one or more cyclic organosilicon compounds, about 5 percent by volume to about 10 percent by volume of one or more aliphatic organosilicon compounds, and about 5 percent by volume to about 35 percent by volume of one or more aliphatic hydrocarbon compounds.

[0035] The one or more cyclic organosilicon compounds are typically introduced to the mixing system 19 at a flow rate of about 100 to about 10,000 sccm, preferably about 520 sccm. The one or more aliphatic organosilicon compounds are introduced to the mixing system 19 at a flow rate of about 100 to about 1,000 sccm, preferably about 600 sccm. The one or more aliphatic hydrocarbon compounds are introduced to the mixing system 19 at a flow rate of about 100 to about 10,000 sccm, preferably about 2,000 sccm. The oxygen containing gas has a flow rate between about 100 and about 6,000 sccm, preferably about 1,000 sccm. One or more organosilicon compounds having a hydrocarbon component having one or

more unsaturated carbon-carbon bonds may be introduced to the mixing system 19 at a flowrate of about 100 sccm to about 10,000 sccm. Preferably, the cyclic organosilicon compound is 1,3,5,7-tetramethylcyclotetrasiloxane, octamethylcyclotetrasiloxane, or a mixture thereof, and the aliphatic organosilicon compound is trimethylsilane, 1,1,3,3-tetramethyldisiloxane, or a mixture thereof. The aliphatic hydrocarbon compound is preferably ethylene.

[0036] In another aspect, the aliphatic hydrocarbons include one or more meta-stable precursors. The one or more meta-stable precursors are added in amounts of about 100 sccm to about 5,000 sccm. Preferably, the meta-stable organic precursor is t-butylether.

[0037] The deposition process can be either a thermal process or a plasma-enhanced process. In a plasma enhanced process, a controlled plasma is typically formed adjacent the substrate by applying RF power to the gas distribution manifold 11 using an RF power supply 25. Alternatively, RF power can be provided to the susceptor 12. The RF power to the deposition chamber may be cycled or pulsed to reduce heating of the substrate and promote greater porosity in the deposited film. The power density of the plasma for a 300 mm substrate is between about 0.014 W/cm^2 and about 2.8 W/cm^2, which corresponds to an RF power level of about 10 W to about 2000 W. Preferably, the RF power level is between about 300 W and about 1700 W.

[0038] The RF power supply 25 can supply a single frequency RF power between about 0.01 MHz and 300 MHz. Alternatively, the RF power may be delivered using mixed, simultaneous frequencies to enhance the decomposition of reactive species introduced into the high vacuum region 15. In one embodiment, the mixed frequency is a lower frequency of about 12 kHz and a higher frequency of about 13.56 MHz. In another embodiment, the lower frequency may range between about 400 kHz and about 14 MHz, and the higher frequency may range between about 20 MHz and about 100 MHz. In another aspect, the lower frequency may range between about 300 Hz to about 1,000 kHz, and the higher frequency may range between about 5 MHz and about 50 MHz.

[0039] During deposition, the substrate is maintained at a temperature between about -20°C and about 500°C, preferably between about 100°C and about 400°C. The deposition pressure is typically between about 0.5 Torr and about 20 Torr, preferably between about 2 Torr and about 8 Torr. The deposition rate is typically between about 5,000 A/min and about 20,000 A/min.

[0040] When remote dissociation of the oxidizing gas is desired, an optional microwave chamber 28 can be used to input power from between about 50 Watts and about 6,000 Watts to the oxidizing gas prior to the gas entering the processing chamber 10. The additional microwave power can avoid excessive dissociation of the organosilicon compounds prior to reaction with the oxidizing gas. A gas distribution plate (not shown) having separate passages for the organosilicon compound and the oxidizing gas is preferred when microwave power is added to the oxidizing gas.

[0041] Typically, any or the entire chamber lining, distribution manifold 11, susceptor 12, and various other reactor hardware are made out of materials such as aluminum or anodized aluminum. An example of such a CVD reactor is described in U.S. Patent No. 5,000,113, entitled "A Thermal CVD/PECVD Reactor and Use for Thermal Chemical Vapor Deposition of Silicon Dioxide and In-situ Multi-step Planarized Process," issued to Wang et al., and assigned to Applied Materials, Inc., the assignee of the invention, and is incorporated by reference herein to the extent not inconsistent with the invention.

[0042] A system controller 34 controls the motor 14, the gas mixing system 19, and the high frequency power supply 25, which are connected therewith by control lines 36. The system controller 34 controls the activities of the CVD reactor and typically includes a hard disk drive, a floppy disk drive, and a card rack. The card rack contains a single board computer (SBC), analog and digital input/output boards, interface boards, and stepper motor controller boards. The system controller 34 conforms to the Versa Modular Europeans (VME) standard, which defines board, card cage, and connector dimensions and types. The VME standard also defines the bus structure having a 16-bit data bus and a 24-bit address bus.

[0043] The pretreatment and method for forming a pretreated layer of the present invention is not limited to any specific apparatus or to any specific plasma excitation method. The above CVD system description is mainly for illustrative purposes, and other CVD equipment such as electrode cyclotron resonance (ECR) plasma CVD devices, induction-coupled RF high density plasma CVD devices, or the like may be employed. Additionally, variations of the above described system such as variations in substrate support pedestal design, heater design, location of power connections and others are possible. For example, the substrate could be supported and heated by a resistively heated substrate support pedestal.

[0044] In any of the embodiments described herein, after the low dielectric constant film is deposited, the film is preferably treated with an electron beam (e-beam). The electron beam treatment typically has a dose between about 50 and about 2000 micro coulombs per square centimeter ($\mu c/cm^2$) at about 1 to 20 kiloelectron volts (KeV). The e-beam treatment is typically operated at a temperature between about room-temperature and about 450°C for about 1 minute to about 15 minutes, such as about 2 minutes. Preferably, the e-beam treatment is performed at about 400°C for about 2 minutes. In one aspect, the e-beam treatment conditions include 4.5 kV, 1.5 mA and 500 $\mu c/cm^2$ at 400°C. Argon or hydrogen may be present during the electron beam treatment. Although any e-beam device may be used, one exemplary device is the EBK chamber, available from Applied Materials, Inc. Treating the low dielectric constant film with an electron beam after the low dielectric constant film is deposited will volatilize at least some of the organic groups in the film, forming voids in the film. Organic groups that may be volatilized are derived from organic components of the precursors described herein, such as the hydrocarbon component of the organosilicon compounds having a hydrocarbon component having one or more unsaturated carbon-carbon bonds, or the aliphatic hydrocarbons described herein. It is believed that forming voids in the film lowers the dielectric constant of the film. Preferably, the film is not deposited at a temperature greater than 150°C, as it is believed that higher temperatures will prevent sufficient incorporation into the film of organic groups that will be volatilized.

[0045] Details of an exemplary e-beam chamber and process will be further described herein. The substrate may be transferred with vacuum break or under

vacuum, i.e., without any vacuum break. Figure 2 illustrates an e-beam chamber 200 in accordance with an embodiment of the invention. The e-beam chamber 200 includes a vacuum chamber 220, a large-area cathode 222, a target plane 230 located in a field-free region 238, and a grid anode 226 positioned between the target plane 230 and the large-area cathode 222. The e-beam chamber 200 further includes a high voltage insulator 224, which isolates the grid anode 226 from the large-area cathode 222, a cathode cover insulator 228 located outside the vacuum chamber 220, a variable leak valve 232 for controlling the pressure inside the vacuum chamber 220, a variable high voltage power supply 229 connected to the large-area cathode 222, and a variable low voltage power supply 231 connected to the grid anode 226.

[0046] The chamber may also include lamps (not shown) that irradiate and heat a substrate, thereby controlling its temperature. The lamps may be located beneath the target plane 230. Since the substrate is in a vacuum environment, and is thermally isolated, the substrate can be heated or cooled by radiation. If the lamps are extinguished, the substrate will radiate away its heat to the surrounding surfaces and gently cool. The substrate may be simultaneously heated by lamps and irradiated by the electron beam throughout the entire process. For example, in accordance with one embodiment, infrared quartz lamps are on continuously until the temperature of the substrate reaches a process operating temperature. Lamps are thereafter turned off and on at varying duty cycle to control the wafer temperature. The substrate is continually irradiated with electrons until a sufficient dose has accumulated and the substrate has been treated. Using this technique, thick layers on the substrate can be cured in, for example, and without limitation, in less than ten minutes.

[0047] In accordance with further embodiments of the present invention, infrared lamps are not used to heat the substrate. In accordance with such embodiments, the electron beam is used to both irradiate and heat the substrate. In this case the product of the beam current and the beam voltage (power=current * voltage) is greater than the power radiated away by the substrate, and therefore the substrate is heated by the electron beam. In accordance with further embodiments of the

present invention, the substrate can be cooled using a cooled plate. This will keep the substrate close to a predetermined temperature.

[0048] In operation, the substrate (not shown) to be exposed with the electron beam is placed on the target plane 230. The vacuum chamber 220 is pumped from atmospheric pressure to a pressure in the range of about 1 mTorr to about 200 mTorr. The exact pressure is controlled by the variable rate leak valve 232, which is capable of controlling pressure to about 0.1 mTorr. The electron beam is generally generated at a sufficiently high voltage, which is applied to the large-area cathode 222 by the high voltage power supply 229. The voltage may range from about -500 volts to about 30,000 volts or higher. The high voltage power supply 229 may be a Bertan Model #105-30R manufactured by Bertan of Hickville, N.Y., or a Spellman Model #SL30N-1200X 258 manufactured by Spellman High Voltage Electronics Corp., of Hauppauge, N.Y. The variable low voltage power supply 231 applies a voltage to the grid anode 226 that is positive relative to the voltage applied to the large-area cathode 222. This voltage is used to control electron emission from the large-area cathode 222. The variable low voltage power supply 231 may be an Acopian Model #150PT12 power supply available from Acopian of Easton, Pa.

[0049] To initiate electron emission, the gas in the field-free region 238 between the grid anode 226 and the target plane 30 must become ionized, which may occur as a result of naturally occurring gamma rays. Electron emission may also be artificially initiated inside the vacuum chamber 220 by a high voltage spark gap. Once this initial ionization takes place, positive ions 342 (shown in Figure 3) are attracted to the grid anode 226 by a slightly negative voltage, i.e., on the order of about 0 to about -200 volts, applied to the grid anode 226. These positive ions 342 pass into the accelerating field region 236, disposed between the large-area cathode 222 and the grid anode 226, and are accelerated towards the large-area cathode 222 as a result of the high voltage applied to the large-area cathode 222. Upon striking the large-area cathode 222, these high-energy ions produce secondary electrons 344, which are accelerated back toward the grid anode 226. Some of these electrons 344, which travel generally perpendicular to the cathode surface, strike the grid anode 226, but many of these electrons 344 pass through the grid anode 226 and travel to the target plane 230. The grid anode 226 is

preferably positioned at a distance less than the mean free path of the electrons emitted by the large-area cathode 222, e.g., the grid anode 226 is preferably positioned less than about 4 mm from the large-area cathode 222. Due to the short distance between the grid anode 226 and the large-area cathode 222, no, or minimal if any, ionization takes place in the accelerating field region 236 between the grid anode 226 and the large-area cathode 222.

[0050] In a conventional gas discharge device, the electrons would create further positive ions in the accelerating field region, which would be attracted to the large-area cathode 222, creating even more electron emission. The discharge could easily avalanche into an unstable high voltage breakdown. However, in accordance with an embodiment of the invention, the ions 342 created outside the grid anode 226 may be controlled (repelled or attracted) by the voltage applied to the grid anode 226. In other words, the electron emission may be continuously controlled by varying the voltage on the grid anode 226. Alternatively, the electron emission may be controlled by the variable leak valve 232, which is configured to raise or lower the number of molecules in the ionization region between the target plane 230 and the large-area cathode 222. The electron emission may be entirely turned off by applying a positive voltage to the grid anode 226, i.e., when the grid anode voltage exceeds the energy of any of the positive ion species created in the space between the grid anode 226 and target plane 230.

[0051] Figure 4 illustrates the e-beam chamber 200 with a feedback control circuit 400. In some applications it may be desirable to provide a constant beam current at different electron beam energies. For example, it may be desirable to expose or cure the upper layer of the film formed on the substrate, but not the bottom layer. This may be accomplished by lowering the electron beam energy such that most of the electrons are absorbed in the upper layer of the film. Subsequent to curing the top layer, it may be desirable to cure the full thickness of the film. This can be done by raising the accelerating voltage of electron beam to penetrate completely through the film. The feedback control circuit 400 is configured to maintain a constant beam current independent of changes in the accelerating voltage. The feedback control circuit 400 includes an integrator 466. The beam current is sampled via a sense resistor 490, which is placed between the

target plane 230 and the integrator 466. The beam current may also be sampled at the grid anode 226 as a portion of the beam is intercepted there. Two unity gain voltage followers 492 buffer the signal obtained across the sense resistor 490 and feed it to an amplifier 496 with a variable resistor 494. The output of this amplifier controls the voltage on the grid anode 226 such that an increase in beam current will cause a decrease in bias voltage on the grid anode 226 and a decrease in beam current from the large-area cathode 222. The gain of the amplifier 496 is adjusted, by means of the variable resistor 494, so that any change in beam current caused by a change in the accelerating voltage is counteracted by a change in bias voltage, thereby maintaining a constant beam current at the target. Alternatively, the output of the amplifier 496 may be connected to a voltage controlled variable rate leak valve 298 to counteract changes in beam current by raising or lowering the pressure in the ionization region 238. Further, a wider range of beam current control may be provided by utilizing feedback signals to both the variable leak valve 298 and the grid anode 226. Other details of the e-beam chamber 200 are described in U.S. Pat. No. 5,003,178, entitled "Large-Area Uniform Electron Source", issued to William R. Livesay, assigned to Electron Vision Corporation (which is currently owned by the assignee of the present invention) and is incorporated by reference herein to the extent not inconsistent with the invention.

[0052] Process conditions for e-beam treatment include the following. The pressure in the chamber may vary in a range of from about 10^{-5} to about 10^{2} Torr, and preferably in a range of from about 10^{-3} to 10^{-1} Torr. The distance between substrate and grid anode should be sufficient for electrons to generate ions in their transit between grid anode and the surface of substrate. The temperature of wafer may vary in a range from about 0°C to about 1050°C. The electron beam energy may vary in a range from about 0.1 to about 100 KeV. The total dose of electrons may vary in a range from about 1 to about 100,000 $\mu C/cm^2$. The dose and energy selected will be proportional to the thickness of the films to be treated. The gas ambient in e-beam tool apparatus may be any of the following gases: nitrogen, oxygen, hydrogen, argon, helium, ammonia, silane, xenon or any combination of these gases. The electron beam current may vary in a range from about 0.1 to about 100 mA. Preferably, the e-beam treatment is conducted with a wide, large beam of electrons from a uniform large-area electron beam source which covers the

surface area of the film to be treated. In addition, for thick films, the electron beam dose may be divided into steps of decreasing voltage which provides a uniform dose process in which the material is cured from the bottom up. Thus, the depth of electron beam penetration may be varied during the treatment process. The length of the treatment may range from about 0.5 minute to about 120 minutes As those of ordinary skill in the art can readily appreciate, the length of e-beam treatment may depend one or more of the above-identified parameters, and that particular sets of parameters can be determined routinely without undue experimentation in light of the detailed description presented herein.

[0053] In another embodiment, the temperature at which the e-beam chamber 200 operates ranges from about -200 degrees Celsius to about 600 degrees Celsius, e.g., about 200 degrees Celsius to about 400 degrees Celsius. The electron beam energy ranges from about 0.5 KeV to about 30 KeV. The exposure dose ranges from about 1 $\mu C/cm^2$ to about 400 $\mu C/cm^2$, and more preferably between about 50 to about 200 $\mu C/cm^2$, such as about 70 $\mu C/cm^2$. The electron beams are generally generated at a pressure of about 1 mTorr to about 100 mTorr. The gas ambient in the electron beam chamber 220 may be any of the following gases: nitrogen, oxygen, hydrogen, argon, a blend of hydrogen and nitrogen, ammonia, xenon, or any combination of these gases. The electron beam current ranges from about 1 mA to about 40 mA, and more preferably from about 5 mA to about 20 mA. The electron beam may cover an area from about 4 square inches to about 700 square inches.

[0054] The following embodiments illustrate a low dielectric film with an improved hardness. The film was deposited using a plasma-enhanced chemical vapor deposition chamber. In particular, the film was deposited using a "Producer" system, available from Applied Materials, Inc. of Santa Clara, California.

[0055] The low dielectric constant film was deposited on a 300 mm substrate from the following reactive gases at a chamber pressure of about 5.75 Torr and a substrate temperature of about 400°C.

Octamethylcyclotetrasiloxane (OMCTS), at about 520 sccm;
Trimethylsilane (TMS), at about 600 sccm;
Ethylene, at about 2,000 sccm;

Oxygen, at about 1,000 sccm; and
Helium, at about 1,000 sccm.

[0056] The substrate was positioned 1,050 mils from the gas distribution showerhead. A power level of about 800 W at a frequency of 13.56 MHz was applied to the gas distribution manifold for plasma-enhanced deposition of the film. The film was deposited at a rate of about 12,000 A/min, and had a dielectric constant (k) of about 2.54 measured at 0.1 MHz.

[0057] The film was then treated using an electron beam apparatus, such as the e-beam chamber 200 described above, at the conditions described below for about 90 seconds. During the post treatment, the chamber temperature was about 400 degrees Celsius, the electron beam energy was about 4 KeV, and the electron beam current was about 3 mA. The exposure dose of the electron beam was about 70 $\mu C/cm^2$. Argon was flowed into the chamber at a rate of about 150 sccm for the entire curing process. After the post treatment, the dielectric constant of the film remained about the same, i.e., about 2.54. The hardness of the film increased from about 0.66 GPa to about 1.40 GPa, while the modulus of the film increased from about 4.2 GPa to about 8.3 GPa. The thickness cracking threshold of the film increased from about 8000 Å to about 24,000 Å. The leakage current of the film decreased by at least an order of magnitude, e.g., from about 3.46×10^{-10} A/cm^2 to about 5.72×10^{-11} A/cm^2 (at about 1 MV/cm). The break down voltage of the film increased from about 4.2 MV to about 4.7 MV.

[0058] Further embodiments of the present invention entail fabricating a lower-k dielectric film referred to herein as formulation-II. This film was fabricated wherein the precursors were octamethylcyclotetrasiloxane ("OMCTS:), trimethylsilane ($(CH_3)_3$-SiH), O_2, ethylene (C_2H_4), and He as a diluent. In accordance with one such embodiment, the process conditions were: a flow rate for OMCTS of about 5000 mgm; a flow rate for trimethylsilane of about 600 sccm; a flow rate for O_2 of about 1000 sccm; a flow rate for ethylene of about 2000 sccm; a flow rate for He of about 1000 sccm; a chamber pressure of about 5.75 Torr; a wafer susceptor temperature of about 400°C; a wafer to showerhead spacing of about 1050 mils; and an RF power of about 800 W. Further useful deposition process conditions can be

determined routinely by one of ordinary skill in the art without undue experimentation in light of the detailed description presented herein.

[0059] After this film was deposited, it was e-beam treated. The process conditions were: a treatment dose of about 100 $\mu C/cm^2$ for about 2 min., a chamber pressure for an ambient gas (Ar) of about 15 mTorr, a voltage of about 4.5 KeV, an electron current of about 3 ma, and a wafer temperature of about 400°C. This resulted in a film whose hardness and Young's modulus improved from about 0.699 GPa and about 4.902 GPa for a control wafer (i.e., no e-beam treatment) to about 1.414 GPa and about 9.563 GPa, respectively, for the e-beam treated wafer, while the dielectric constant remained substantially the same, i.e., a k value of about 2.52 for the control wafer vs. a k value of about 2.49 for the e-beam treated wafer. The thickness changed from a nominal value of about 5000 Å (5292.1 Å) for the control wafer to a thickness of about 4889.3 Å for the e-beam treated wafer. These results are important because they show that the e-beam treatment increased the strength of a film which is otherwise mechanically weak, leaving other properties relatively unchanged. A mechanically weak film may be problematic in use in fabricating integrated circuits having many layers such as, for example, logic circuits because stresses which build up due to use of mechanically weak materials may cause stress fractures in upper layers.

[0060] In addition to the above-described improvement for e-beam treated formulation-II, the wetting angle decreased for the e-beam treated wafer; showing that the e-beam treated film became hydrophilic. In particular, the wetting angle changed from a value of over about 80 °C for the control wafer to a value of under about 40 °C for the e-beam treated wafer. This is important because many photoresists will not deposit on a hydrophobic surface.

[0061] Still further embodiments of the present invention entail fabricating a lower-k dielectric film using an oxidizer (such as, for example, and without limitation, H_2O_2, O_3, and so forth) and a stable silicon precursor (such as, for example, and without limitation, tri-methyl silane ("TMS") or tetra-methyl silane or a precursor having a built-in metastable functional group, for example, and without limitation, 1,3,5,7-tetramethylcyclotetrasiloxane (TMCTS). The CVD deposition may take place, for example, and without limitation, using the chamber described above in

conjunction with FIG. 2 at a relatively low temperature. For example, in accordance with one embodiment of the present invention, a process recipe for one such thermal deposition process using TMS and O_3 entails: a chamber pressure of about 100 Torr, a wafer holder temperature of about 100 °C, a flow rate for O_3 of about 4000 sccm, a flow rate of a diluent such as, for example, and without limitation, He, of about 8000 sccm, and a flow rate of TMS of about 125 sccm. Next, the film is e-beam treated (including heating the film at the same time).

[0062] In accordance with one or more embodiments of the present invention, a film is fabricated that includes metastable groups. In accordance with one or more such embodiments, the precursors include vinyl cyclohexane ("VCH"), octamethylcyclotetrasiloxane ("OMCTS"), and He as a diluent, and embodiments of this film were fabricated using the chamber described above in conjunction with FIG. 2. In accordance with one such embodiment, the process conditions were: a flow rate for OMCTS of about 500 mgm, a flow rate for VCH of about 500 mgm, a flow rate for He of about 1000 sccm; a chamber pressure of about 5 Torr; a wafer susceptor temperature of about 100°C; a wafer to showerhead spacing of about 800 mils; and an RF power (13.56 MHz) of about 300 W; and a low frequency power (356 KHz) of about 100 W. The deposition rate for this film was about 12,000 Å/min. Further useful deposition process conditions can be determined routinely by one of ordinary skill in the art without undue experimentation in light of the detailed description presented herein. After this film was deposited it had a refractive index ("RI") equal to about 1.47, and a dielectric constant k equal to about 2.77. The film was thermally annealed for about 30 min. at 440 °C in a furnace. After the thermal anneal, RI was equal to about 1.37, and k was equal to about 2.45.

[0063] After this film was annealed, it was e-beam treated. The process conditions were: a treatment dose of about 200 $\mu C/cm^2$ for about 2 min., a chamber pressure for an ambient gas (Ar) of about 15 mTorr, a voltage of about 4 KeV, an electron current of about 3 ma, and a wafer temperature of about 400°C. This resulted in a film having RI equal to about 1.43, k equal to about 2.46, and increased hardness and Young's modulus.

[0064] In accordance with this approach, further embodiments include the use of precursors that provide metastable species (for example, and without limitation,

cyclohexane or phenyl in the film), and precursors that provide silicon. In accordance with one or more such embodiments, the precursors that provide metastable species include, for example, and without limitation, one or more of norborndiene and butadiene, and the precursors that silicon include, for example, and without limitation, one or more of OMCTS, TMCTS, DMDMOS, and DEMS (Si singly bonded to H, CH_3, and $(OC_2H_5)_2$). In accordance with this approach, still further embodiments include the use of precursors where the metastable functional group can be attached to an organic compound, for example, VCH, or it can be built into a silicon precursor, for example, t-butyl TMCTS.

[0065] Further embodiments of the present invention entail carrying out multiple process step cycles (i.e., thermal deposition/e-beam treatment process step cycles). Finally, and optionally, the resulting film is thermally annealed. In accordance with one such embodiment, the e-beam treatment steps are short to reduce shrinkage and to obtain k values <2.5.

[0066] In accordance with another embodiment of the present invention, any of the above-described embodiments may be followed by further treatment processes, prior to and/or after, the optional thermal anneal step, to further harden such organo-silicon-based films. For example, and without limitation, such further treatment processes may include exposure to relatively inert plasmas such as He or H_2 plasmas. However, in the absence of penetration throughout the film by higher energy electrons, such effects, for example, hardening, may be linked largely to changes in surface composition induced by sputtering away of organic constituents by ions rather than the cross-linking processes believed to be operative during e-beam treatment. However, for very thin barrier films containing sufficiently high carbon content, the use of such processes can also be advantageous. In accordance with one or more such embodiments, the plasma treatment may be carried out in conventional PECVD or plasma etch hardware.

[0067] <u>Examples:</u>

[0068] <u>Hypothetical Example 1</u>

[0069] A low dielectric constant film is deposited on a 200 mm substrate from the following reactive gases at a chamber pressure of about 6 Torr and a substrate temperature of about 100°C.

Octamethylcyclotetrasiloxane (OMCTS), at about 520 sccm;
Ethylene, at about 2,000 sccm;
Oxygen, at about 1,000 sccm; and
Helium, at about 1,000 sccm

[0070] The substrate is positioned 1,050 mils from the gas distribution showerhead. A power level of about 1200 W at a frequency of 13.56 MHz is applied to the showerhead for plasma enhanced deposition of the film. After the low dielectric constant film is deposited, the substrate is treated with electron beam exposure at about 400°C with about 50 $\mu c/cm^2$ dosage in an EBK chamber. Argon is introduced into the chamber at a rate of about 200 sccm. The chamber pressure is maintained at about 35 mTorr.

[0071] <u>Hypothetical Example 2</u>

[0072] A low dielectric constant film is deposited on a 200 mm substrate from the following reactive gases at a chamber pressure of about 14 Torr and a substrate temperature of about 125°C.

Octamethylcyclotetrasiloxane (OMCTS), at about 210 sccm;
Diethoxymethylsilane, at about 600 sccm;
1,3-butadiene, at about 1,000 sccm;
Oxygen, at about 600 sccm; and
Helium, at about 800 sccm

[0073] The substrate is positioned 1,050 mils from the gas distribution showerhead. A power level of about 1200 W at a frequency of 13.56 MHz is applied to the showerhead for plasma enhanced deposition of the film. After the low dielectric constant film is deposited, the substrate is treated with electron beam exposure at about 400°C with about 50 $\mu c/cm^2$ dosage in an EBK chamber. Argon

is introduced into the chamber at a rate of about 200 sccm. The chamber pressure is maintained at about 35 mTorr.

[0074] **Hypothetical Example 3**

[0075] A low dielectric constant film is deposited on a 200 mm substrate from the following reactive gases at a chamber pressure of about 6 Torr and a substrate temperature of about 125°C.

Octamethylcyclotetrasiloxane (OMCTS), at about 520 sccm;
Propylene, at about 2,000 sccm;
Oxygen, at about 1,000 sccm; and
Helium, at about 1,000 sccm

[0076] The substrate is positioned 1,050 mils from the gas distribution showerhead. A power level of about 800 W at a frequency of 13.56 MHz is applied to the showerhead for plasma enhanced deposition of the film. After the low dielectric constant film is deposited, the substrate is annealed at a temperature between about 200°C and about 400°C for about 30 minutes. A non-reactive gas such as helium, hydrogen, nitrogen, or a mixture thereof is introduced into the chamber at a rate of 100 to about 10,000 sccm. The chamber pressure is maintained between about 2 Torr and about 10 Torr. The RF power is about 200 W to about 1,000 W at a frequency of about 13.56 MHz, and the preferable substrate spacing is between about 300 mils and about 800 mils.

[0077] **Hypothetical Example 4**

[0078] A low dielectric constant film is deposited on a 200 mm substrate from the following reactive gases at a chamber pressure of about 6 Torr and a substrate temperature of about 100°C.

1,3,5,7-tetramethylcyclotetrasiloxane (TMCTS), at about 700 sccm;
Diethoxymethylsilane, at about 600 sccm;
2,3-dimethyl-1,3-butadiene, at about 2,000 sccm;
Oxygen, at about 1,000 sccm; and

Helium, at about 1,000 sccm

[0079] The substrate is positioned 1,050 mils from the gas distribution showerhead. A power level of about 800 W at a frequency of 13.56 MHz is applied to the showerhead for plasma enhanced deposition of the film. After the low dielectric constant film is deposited, the substrate is annealed at a temperature between about 200°C and about 400°C for about 30 minutes. A non-reactive gas such as helium, hydrogen, nitrogen, or a mixture thereof is introduced into the chamber at a rate of 100 to about 10,000 sccm. The chamber pressure is maintained between about 2 Torr and about 10 Torr. The RF power is about 700 W to about 1,000 W at a frequency of about 13.56 MHz, and the preferable substrate spacing is between about 300 mils and about 800 mils.

[0080] <u>Hypothetical Example 5</u>

[0081] A low dielectric constant film is deposited on a substrate from the following reactive gases at a chamber pressure of about 6 Torr and a substrate temperature of about 130°C.

Vinylmethylsilane, at about 600 sccm;
Oxygen, at about 800 sccm; and
Carbon dioxide, at about 4,800 sccm

[0082] The substrate is positioned 1,050 mils from the gas distribution showerhead. A power level of about 1200 W at a frequency of 13.56 MHz is applied to the showerhead for plasma enhanced deposition of the film. After the low dielectric constant film is deposited, the substrate is treated with electron beam exposure at about 400°C with about 50 $\mu c/cm^2$ dosage in an EBK chamber. Argon is introduced into the chamber at a rate of about 200 sccm. The chamber pressure is maintained at about 35 mTorr.

[0083] <u>Hypothetical Example 6</u>

[0084] A low dielectric constant film is deposited on a 300 mm substrate from the following reactive gases at a chamber pressure of about 6 Torr and a substrate temperature of about 130°C.

Octamethylcyclotetrasiloxane (OMCTS), at about 483 sccm;
Ethylene, at about 1,600 sccm;
Carbon dioxide, at about 4,800 sccm;
Oxygen, at about 800 sccm; and
Argon, at about 1,600 sccm

[0085] The substrate is positioned 1,050 mils from the gas distribution showerhead. A power level of about 800 W at a frequency of 13.56 MHz is applied to the showerhead for plasma enhanced deposition of the film. After the low dielectric constant film is deposited, the substrate is treated with electron beam exposure at about 400°C and 1.5 mA with about 70 $\mu c/cm^2$ dosage in an EBK chamber.

[0086] The following examples illustrate low dielectric films of the present invention. The films were deposited using a chemical vapor deposition chamber that is part of an integrated processing platform. In particular, the films were deposited using a Producer® system, available from Applied Materials, Inc. of Santa Clara, California.

[0087] **Example 1:**

[0088] A low dielectric constant film was deposited on a 200 mm substrate from the following reactive gases at a chamber pressure of about 6 Torr and substrate temperature of about 400°C.

Octamethylcyclotetrasiloxane (OMCTS), at about 520 sccm;
Trimethylsilane (TMS), at about 200 sccm;
Ethylene, at about 2,000 sccm;
Oxygen, at about 1,000 sccm; and
Helium, at about 1,000 sccm

[0089] The substrate was positioned 1,050 mils from the gas distribution showerhead. A power level of about 800 W at a frequency of 13.56 MHz was applied to the showerhead for plasma enhanced deposition of the film. The film was deposited at a rate of about 12,000 Å/min, and had a dielectric constant (k) of about 2.54 measured at 0.1 MHz.

[0090] **Example 2:**

[0091] A low dielectric constant film was deposited on a 200 mm substrate from the following reactive gases at a chamber pressure of about 6 Torr and substrate temperature of about 400°C.

Octamethylcyclotetrasiloxane (OMCTS), at about 520 sccm;
Trimethylsilane (TMS), at about 400 sccm;
Ethylene, at about 2,000 sccm;
Oxygen, at about 1,000 sccm; and
Helium, at about 1,000 sccm;

[0092] The substrate was positioned 1,050 mils from the gas distribution showerhead. A power level of about 800 W at a frequency of 13.56 MHz was applied to the showerhead for plasma enhanced deposition of the film. The film was deposited at a rate of about 12,000 Å/min, and had a dielectric constant (k) of about 2.51 measured at 0.1 MHz.

[0093] **Example 3:**

[0094] A low dielectric constant film was deposited on a 200 mm substrate from the following reactive gases at a chamber pressure of about 6 Torr and substrate temperature of about 400°C.

Octamethylcyclotetrasiloxane (OMCTS), at about 520 sccm;
Trimethylsilane (TMS), at about 600 sccm;
Ethylene, at about 2,000 sccm;
Oxygen, at about 1,000 sccm; and
Helium, at about 1,000 sccm

[0095] The substrate was positioned 1,050 mils from the gas distribution showerhead. A power level of about 800 W at a frequency of 13.56 MHz was applied to the showerhead for plasma enhanced deposition of the film. The film was deposited at a rate of about 12,000 Å/min, and had a dielectric constant (k) of about 2.47 measured at 0.1 MHz.

[0096] **Example 4:**

[0097] A low dielectric constant film was deposited on a 200 mm substrate from the following reactive gases at a chamber pressure of about 6 Torr and substrate temperature of about 400°C.

Octamethylcyclotetrasiloxane (OMCTS), at about 520 sccm;
Trimethylsilane (TMS), at about 800 sccm;
Ethylene, at about 2,000 sccm;
Oxygen, at about 1,000 sccm; and
Helium, at about 1,000 sccm

[0098] The substrate was positioned 1,050 mils from the gas distribution showerhead. A power level of about 800 W at a frequency of 13.56 MHz was applied to the showerhead for plasma enhanced deposition of the film. The film was deposited at a rate of about 12,000 Å/min, and had a dielectric constant (k) of about 2.47 measured at 0.1 MHz.

[0099] **Example 5:**

[00100] A low dielectric constant film was deposited on a 200 mm substrate from the following reactive gases at a chamber pressure of about 6 Torr and substrate temperature of about 400°C.

Octamethylcyclotetrasiloxane (OMCTS), at about 520 sccm;
Trimethylsilane (TMS), at about 900 sccm;
Ethylene, at about 2,000 sccm;
Oxygen, at about 1,000 sccm; and
Helium, at about 1,000 sccm

[00101] The substrate was positioned 1,050 mils from the gas distribution showerhead. A power level of about 800 W at a frequency of 13.56 MHz was applied to the showerhead for plasma enhanced deposition of the film. The film was deposited at a rate of about 12,000 Å/min, and had a dielectric constant (k) of about 2.48 measured at 0.1 MHz.

[00102] **Example 6:**

[00103] A low dielectric constant film was deposited on a substrate from the following reactive gases at a chamber pressure of about 14 Torr and substrate temperature of 350°C.

Octamethylcyclotetrasiloxane (OMCTS), at about 210 sccm;
Trimethylsilane (TMS), at about 400 sccm;
Oxygen, at about 600 sccm; and
Helium, at about 800 sccm

[00104] The substrate was positioned 450 mils from the gas distribution showerhead. A power level of 800 W at a frequency of 13.56 MHz was applied to the showerhead for plasma enhanced deposition of the film. The deposited film had a dielectric constant (k) of about 2.67 measured at 0.1 MHz.

[00105] **Example 7:**

[00106] A low dielectric constant film was deposited on a substrate from the following reactive gases at a chamber pressure of about 6 Torr and substrate temperature of 400°C.

Octamethylcyclotetrasiloxane (OMCTS), at about 520 sccm;
Ethylene, at about 2,000 sccm;
Oxygen, at about 1,000 sccm; and
Helium, at about 1,000 sccm

[00107] The substrate was positioned 1,050 mils from the gas distribution showerhead. A power level of 800 W at a frequency of 13.56 MHz was applied to

the showerhead for plasma enhanced deposition of the film. The deposited film had a dielectric constant (k) of about 2.55 measured at 0.1 MHz.

[00108] **Example 8:**

[00109] A low dielectric constant film was deposited on a substrate from the following reactive gases at a chamber pressure of about 6 Torr and substrate temperature of 130°C.

Octamethylcyclotetrasiloxane (OMCTS), at about 483 sccm;
Ethylene, at about 3200 sccm;
Oxygen, at about 800 sccm; and
Carbon dioxide, at about 4800 sccm

[00110] The substrate was positioned 1050 mils from the gas distribution showerhead. A power level of about 1200 W at a frequency of 13.56 MHz was applied to the showerhead for plasma enhanced deposition of the film. After the low dielectric constant film was deposited, the substrate was treated with electron beam exposure at about 400°C with about 50 $\mu c/cm^2$ dosage in an EBK chamber. Argon was introduced into the chamber at a rate of about 200 sccm. The chamber pressure was maintained at about 35 mTorr.

[00111] **Example 9:**

[00112] Low dielectric constant films were deposited on 300 mm substrates from the following reactive gases at a chamber pressure of about 5 Torr and substrate temperature of 400°C.

Octamethylcyclotetrasiloxane (OMCTS), at about 302 sccm;
Trimethylsilane, at about 600 sccm;
Oxygen, at about 600 sccm;
Ethylene, at about 1000 sccm; and
Helium, at about 1200 sccm

[00113] The substrates were positioned 350 mils from the gas distribution showerhead. A power level of about 800 W at a frequency of 13.56 MHz and a

power level of about 250 W at a frequency of 356 kHz were applied for plasma enhanced deposition of the films. After the low dielectric constant films were deposited, the substrates were post-treated with helium. The films were deposited at a rate of 13,000 Å/min and had an average dielectric constant of about 2.97 to about 3.06. The average refractive index was 1.453. The hardness of the films was about 2.2 gPa, and the uniformity was less than 2%. The modulus was about 13.34. The leakage current was about 4.55×10^{-10} amp/cm^2 at 1 MV/cm. The leakage current was about 2.68×10^{-9} amp/cm^2 at 2 MV/cm. The breakdown voltage was about 5.93 MV/cm. The stress was about 4.00×10^{8} dynes/cm^2, and the cracking threshold was greater than 7 μm.

[00114] **Example 10:**

[00115] Low dielectric constant films were deposited on 200 mm substrates from the following reactive gases at a chamber pressure of about 4.5 Torr and substrate temperature of 400°C.

Octamethylcyclotetrasiloxane (OMCTS), at about 151 sccm;
Trimethylsilane, at about 300 sccm;
Oxygen, at about 300 sccm;
Ethylene, at about 500 sccm; and
Helium, at about 600 sccm

[00116] The substrates were positioned 350 mils from the gas distribution showerhead. A power level of about 400 W at a frequency of 13.56 MHz and a power level of about 150 W at a frequency of 356 kHz were applied for plasma enhanced deposition of the films. After the low dielectric constant films were deposited, the substrates were post-treated with hydrogen. The films were deposited at a rate of 10,000 Å/min and had an average dielectric constant of about 2.96 to about 3.01. The average refractive index was 1.454. The hardness of the films was about 2.03 to about 2.08 gPa, and the uniformity was 2.2%. The modulus was about 12.27. The leakage current was about 4.27×10^{-10} amp/cm^2 at 2 MV/cm. The leakage current was about 1.88×10^{-9} amp/cm^2 at 2 MV/cm. The breakdown voltage was about 4.31 MV/cm. The stress was about 5.40×10^{8} dynes/cm^2, and the cracking threshold was greater than 7 μm.

[00117] While Examples 9 and 10 use helium as a carrier gas, argon may also be used as the carrier gas. It is believed that the use of argon as a carrier gas increases the porosity of the deposited film and lowers the dielectric constant of the deposited film. It is believed that the use of argon and mixed frequency RF power increases the deposition rate of the films by improving the efficiency of precursor dissociation. Additionally, it is believed that the use of argon and mixed frequency RF power enhances the hardness and modulus strength of the films without increasing the dielectric constant of the films. Furthermore, it is believed that the use of argon and mixed frequency RF power reduces the beveled deposition of material that may occur at the edge of a substrate.

[00118] It was surprisingly found that the dielectric constant significantly decreased as the flow rate of TMS increased between about 200 sccm to about 600 sccm in Examples 1-5. The low dielectric constants were achieved with a ratio of aliphatic hydrocarbon compound to aliphatic organosilicon compound of about 15:1 to about 1:1. As illustrated with Example 6, the addition of a sufficient amount of the aliphatic hydrocarbon compound to the cyclic organosilicon and aliphatic organosilicon compounds provided a dielectric constant at least 7% lower than a dielectric constant obtained by omitting the aliphatic hydrocarbon compound. Further, the addition of a sufficient amount of the aliphatic organosilicon compound to the cyclic organosilicon and aliphatic hydrocarbon compounds provided a dielectric constant about 3% lower than a dielectric constant obtained by omitting the aliphatic organosilicon compound as shown in Example 7.

[00119] The following examples illustrate the low dielectric films of the present invention. The films were deposited on 200 mm substrates using a chemical vapor deposition chamber, such as the "Producer DxZ" system, available from Applied Materials, Inc. of Santa Clara, California.

[00120] **Example 11:**

[00121] A low dielectric constant film was deposited on each of three 200 mm substrates at about 8 Torr and temperature of about 200°C. The following processing gases and flow rates were used:

Alpha-terpinene (ATP), at 3,000 mgm;

Diethoxymethylsilane (DEMS), at 800 mgm; and

Carbon dioxide, at 1,000 sccm.

[00122] Each substrate was positioned 300 mils from the gas distribution showerhead. A power level of 600 W at a frequency of 13.56 MHz was applied to the showerhead for plasma enhanced deposition of the films. Each film was deposited at a rate of about 2,700 A/min, and had a dielectric constant (k) of about 5.4 measured using SSM 5100 Hg CV measurement tool at 0.1 MHz. Each film also exhibited a hardness of about 0.1 GPa.

[00123] <u>Thermal Anneal:</u>

[00124] The first deposited film was subjected to a thermal anneal process. The anneal treatment utilized a temperature of about 425°C at a pressure of about 10 Torr in an inert gas environment for about 4 hours. Shorter anneal times resulted in higher k values. The thermally annealed film had a lowest k value of about 2.1 and a hardness of about 0.2 GPa.

[00125] <u>E-BEAM @ 400°C:</u>

[00126] The second deposited film was subjected to a high temperature electron beam (e-beam) treatment using a dose of about 300 $\mu c/cm^2$, at about 4.5 KeV and 1.5 mA, and at about 400°C. The e-beam treatment lasted for about 2 minutes. Following the e-beam treatment, the film exhibited a dielectric constant of about 2.1 which is about 60% less than the non-cured films and similar to the lowest value of the thermally annealed film. The e-beam film also exhibited a hardness of about 0.7 GPa, which is about an 600% increase compared to the non-cured films, and a 250% increase compared to the thermally annealed film.

[00127] <u>E-BEAM AT ROOM TEMPERATURE:</u>

[00128] The third deposited film was subjected to a low temperature electron beam (e-beam) treatment using a dose of about 300 $\mu c/cm^2$, at about 4.5 KeV and 1.5 mA, and at about 35°C. The e-beam treatment lasted for about 2 minutes. Following the e-beam treatment, the film exhibited a dielectric constant of about 2.3 which is about 57% less than the non-cured films. The e-beam film also exhibited a

hardness of about 0.5 GPa, which is about an 400% increase compared to the non-cured films, and a 150% increase compared to the thermally annealed film.

[00129] **Example 12:**

[00130] A low dielectric constant film was deposited on each of three substrates at about 8 Torr and temperature of about 225°C. The following processing gases and flow rates were used:

Alpha-terpinene (ATP), at 3,000 mgm;
Diethoxymethylsilane (DEMS), at 800 mgm;
Carbon dioxide, at 1,500 sccm; and
Oxygen, at 100 sccm.

[00131] Each substrate was positioned 300 mils from the gas distribution showerhead. A power level of 600 W at a frequency of 13.56 MHz was applied to the showerhead for plasma enhanced deposition of the films. Each film was deposited at a rate of about 1,800 A/min, and had a dielectric constant (k) of about 2.85 measured using SSM 5100 Hg CV measurement tool at 0.1 MHz. Each film also exhibited a hardness of about 0.23 GPa.

[00132] Thermal Anneal:

[00133] The first deposited film was subjected to a thermal anneal process. The anneal treatment utilized a temperature of about 450°C at a pressure of about 10 Torr in an inert gas environment for about 30 minutes. Shorter anneal times resulted in higher k values. The thermally annealed film had a refractory index (RI) of about 1.29, a lowest k value of about 2.08, and a hardness of about 0.23 GPa.

[00134] E-BEAM @ 400°C and 200 $\mu c/cm^2$:

[00135] The second deposited film was subjected to a high temperature electron beam (e-beam) treatment using a dose of about 200 $\mu c/cm^2$, at about 4.5 KeV and 1.5 mA, and at about 400°C. The e-beam treatment lasted for about 100 seconds.

Following the e-beam treatment, the film exhibited a dielectric constant of about 2.07 which is about 27 % less than the non-cured films and similar to the lowest value of the thermally annealed film. The e-beam film also exhibited a hardness of about 0.42 GPa, which is about an 80% increase compared to the non-cured films and the thermally annealed film.

[00136] E-BEAM @ 400°C and 500 $\mu c/cm^2$:

[00137] The third deposited film was subjected to a low temperature electron beam (e-beam) treatment using a dose of about 500 $\mu c/cm^2$, at about 4.5 KeV and 1.5 mA, and at about 35°C. The e-beam treatment lasted for about 250 seconds. Following the e-beam treatment, the film exhibited a dielectric constant of about 2.14 which is about 25% less than the non-cured films. The e-beam film also exhibited a hardness of about 0.74 GPa, which is about a 220% increase compared to the non-cured films and the thermally annealed film.

[00138] **Example 13:**

[00139] A low dielectric constant film was deposited on each of two substrates at about 8 Torr and a temperature of about 225°C. The following processing gases and flow rates were used:

Alpha-terpinene (ATP), at 4,000 mgm;
Octamethylcyclotetrasiloxane (OMCTS), at 200 mgm;
Oxygen, at 200 sccm; and
Carbon dioxide 2,000 sccm.

[00140] Each substrate was positioned about 300 mils from the gas distribution showerhead. A power level of 500 W at a frequency of 13.56 MHz was applied o the showerhead for plasma enhanced deposition of the films. Each film was deposited at a rate of about 1,000 A/min, and had a dielectric constant (k) of about 4.0 measured using SSM 5100 Hg CV measurement tool at 0.1 MHz. Each film also exhibited a hardness of about 0.1 GPa.

[00141] E-BEAM @ 400°C and 120 micro c/cm^2:

[00142] The first deposited film was subjected to a high temperature electron beam (e-beam) treatment using a dose of about 120 micro c/cm2, at about 4.5 KeV and 1.5 mA, and at about 400°C. The e-beam treatment lasted for about 30 seconds. Following the e-beam treatment, the film exhibited a dielectric constant of about 1.9 which is about 52 % less than the non-cured films. The e-beam film also exhibited a hardness of about 0.5 GPa, which is about a 400% increase compared to the non-cured films.

[00143] E-BEAM @ 400°C and 600 micro c/cm^2:

[00144] The second deposited film was subjected to a low temperature electron beam (e-beam) treatment using a dose of about 600 micro c/cm2, at about 4.5 KeV and 1.5 mA, and at about 400°C. The e-beam treatment lasted for about 150 seconds. Following the e-beam treatment, the film exhibited a dielectric constant of about 2.2, which is about 45% less than the non-cured films. The e-beam film also exhibited a hardness of about 0.8 GPa, which is about a 700% increase compared to the non-cured films.

[00145] **Example 14:**

[00146] A low dielectric constant film was deposited on a substrate at about 8 Torr and a temperature of about 225°C. The following processing gases and flow rates were used:

ATP, at 3,000 mgm;
TMS, at 500 sccm;
DEMS, at 600 mgm;
Oxygen, at 100 sccm; and
Carbon dioxide, at 1,500 sccm.

[00147] The substrate was positioned about 300 mils from the gas distribution showerhead. A power level of 600 W at a frequency of 13.56 MHz was applied o the showerhead for plasma enhanced deposition of the films. The film was deposited at a rate of about 2,000 A/min, and had a dielectric constant (k) of about 4.3 measured using SSM 5100 Hg CV measurement tool at 0.1 MHz. The film also exhibited a hardness of about 0.1 GPa.

[00148] E-BEAM @ 400°C and 200 micro c/cm^2:

[00149] The deposited film was subjected to a high temperature electron beam (e-beam) treatment using a dose of about 200 micro c/cm2, at about 4.5 KeV and 1.5 mA, and at about 400°C. The e-beam treatment lasted for about 30 seconds. Following the e-beam treatment, the film exhibited a dielectric constant of about 2.2 which is about 50 % less than the non-cured film. The e-beam film also exhibited a hardness of about 0.7 GPa, which is about a 600% increase compared to the non-cured film.

[00150] **Example 15:**

[00151] A low dielectric constant film was deposited on a substrate at about 8 Torr and a temperature of about 225°C. The following processing gases and flow rates were used:

ATP, at 4,000 mgm;
TMS, at 1,000 sccm;
OMCTS, at 200 mgm
Oxygen, at 100 sccm; and
Carbon dioxide, at 1,500 sccm.

[00152] The substrate was positioned about 300 mils from the gas distribution showerhead. A power level of 500 W at a frequency of 13.56 MHz was applied o the showerhead for plasma enhanced deposition of the films. The film was deposited at a rate of about 1,600 A/min, and had a dielectric constant (k) of about 4.5 measured using SSM 5100 Hg CV measurement tool at 0.1 MHz. The film also exhibited a hardness of about 0.1 GPa.

[00153] E-BEAM @ 400°C and 200 micro c/cm^2:

[00154] The deposited film was subjected to a high temperature electron beam (e-beam) treatment using a dose of about 200 micro c/cm2, at about 4.5 KeV and 1.5 mA, and at about 400°C. The e-beam treatment lasted for about 30 seconds. Following the e-beam treatment, the film exhibited a dielectric constant of about 2.3 which is about 50 % less than the non-cured film. The e-beam film also exhibited a

hardness of about 0.7 GPa, which is about a 600% increase compared to the non-cured film.

[00155] While the foregoing is directed to embodiments of the present invention, other and further embodiments of the invention may be devised without departing from the basic scope thereof, and the scope thereof is determined by the claims that follow.

What is Claimed is:

1. A method for depositing a low dielectric constant film on a substrate, comprising:

depositing a low dielectric constant film comprising silicon, carbon, oxygen and hydrogen in a chemical vapor deposition chamber; and

exposing the low dielectric constant film to an electron beam at conditions sufficient to increase the hardness of the low dielectric constant film.

2. The method of claim 1, wherein the chemical vapor deposition chamber is a plasma-enhanced chemical vapor deposition chamber.

3. The method of claim 1, wherein the depositing comprises:

introducing a gas mixture into the plasma-enhanced chemical vapor deposition chamber, the gas mixture comprising one or more compounds selected from a group consisting of cyclic organosilison compounds, aliphatic organosilicon compounds, hydrocarbon compounds, and oxidizing gases; and

reacting the gas mixture to form the low dielectric constant film on the substrate.

4. The method of claim 1, wherein the conditions comprise an electron beam current ranging from about 1 mA to about 15 mA.

5. The method of claim 1, wherein the exposure dose of the electron beam is between about 50 $\mu C/cm^2$ to about 400 $\mu C/cm^2$.

6. The method of claim 1, further comprising flowing argon gas at a rate of about 150 sccm across the low dielectric constant film.

7. The method of claim 1, wherein the organosilicon compounds comprise at least one silicon-carbon bond and at least one silicon-hydrogen bond.

8. The method of claim 1, wherein the hydrocarbon compounds comprise an unsaturated carbon-carbon bond.

9. A method for depositing a low dielectric constant film, comprising:

delivering a gas mixture comprising one or more organosilicon compounds and one or more hydrocarbon compounds having at least one cyclic group to a substrate surface at deposition conditions sufficient to deposit a non-cured film comprising the at least one cyclic group on the substrate surface and having a hardness less than about 0.3 GPa; and

substantially removing the at least one cyclic group from the non-cured film using an electron beam at curing conditions sufficient to provide a dielectric constant less than 2.5 and a hardness greater than 0.5 GPa.

10. The method of claim 9, wherein the one or more organosilicon compounds has an oxygen to silicon ratio of at least 2:1.

11. The method of claim 9, wherein the at least one cyclic group is a partially saturated ring of five or six carbon atoms.

12. The method of claim 9, wherein the one or more compounds having at least one cyclic group comprises alpha-terpinene.

13. The method of claim 9, wherein the curing conditions comprise an electron beam dosage from about 200 to about 400 micro coulombs per cm^2.

14. A method for depositing a low dielectric constant film, comprising:

delivering a gas mixture comprising one or more organosilicon compounds, one or more hydrocarbon compounds having at least one cyclic group, and two or more oxidizing gases to a substrate surface at deposition conditions sufficient to deposit a non-cured film comprising the at least one cyclic group on the substrate surface and having a hardness less than 0.3 GPa; and

substantially removing the at least one cyclic group from the non-cured film using an electron beam at curing conditions sufficient to provide a dielectric constant less than 2.2 and a hardness greater than 0.4 GPa.

15. The method of claim 14, wherein the two or more the oxidizing gas comprises oxygen and carbon dioxide.

16. A method for depositing a low dielectric constant film having a dielectric constant of about 3.0 or less, comprising:

reacting a gas mixture comprising:

one or more organosilicon compounds;

one or more aliphatic hydrocarbon compounds having one or more unsaturated carbon-carbon bonds; and

one or more oxidizing gases;

delivering the gas mixture to a substrate surface at conditions sufficient to deposit the low dielectric constant film on the substrate surface; and

post-treating the low dielectric constant film with an electron beam to reduce the dielectric constant of the film.

17. The method of claim 16, wherein the one or more organosilicon compounds comprises at least one silicon-carbon bond and at least one silicon-hydrogen bond.

18. The method of claim 16, wherein the aliphatic hydrocarbon compound comprises two or more unsaturated carbon-carbon bonds.

19. The method of claim 16, wherein the conditions comprise mixed frequency RF power having a frequency of 13.56 MHz and a frequency of 356 kHz.

20. The method of claim 16, wherein the gas mixture further comprises argon.

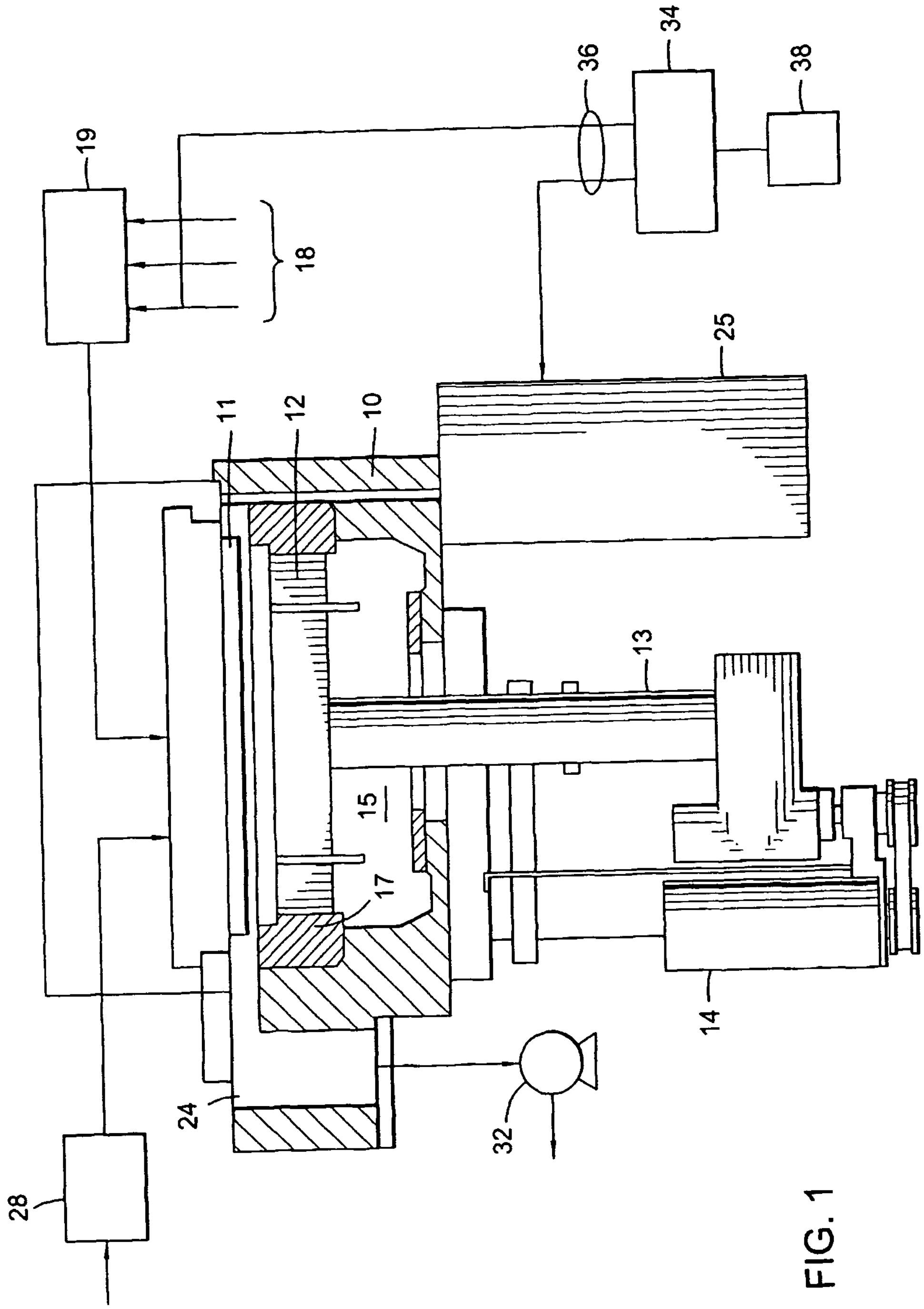
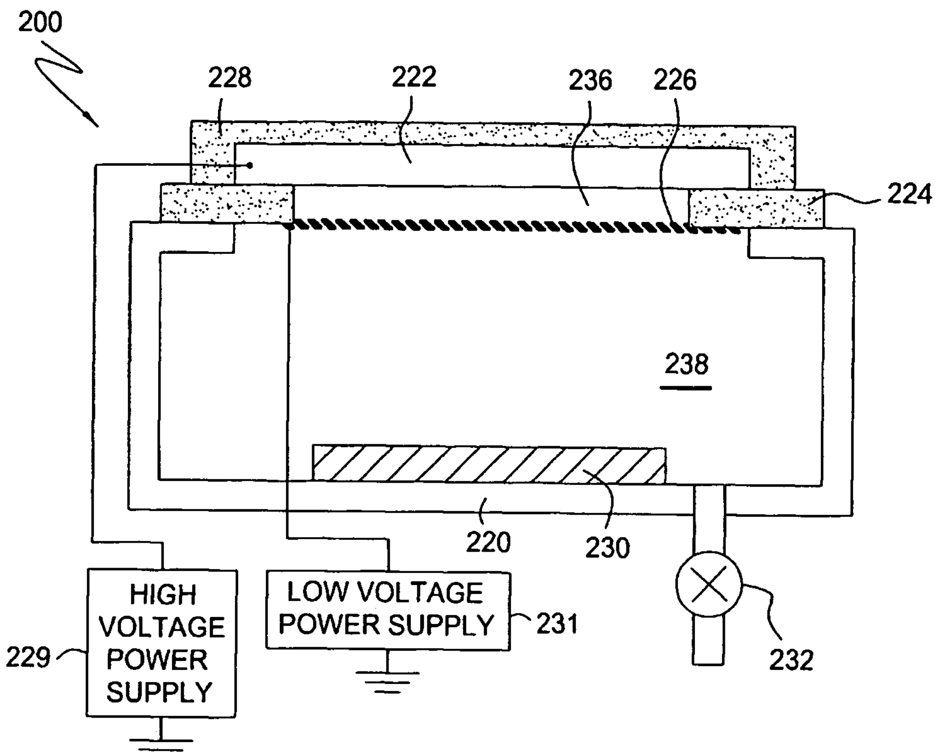


FIG. 1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HIGH VOLTAGE POWER SUPPLY
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LOW VOLTAGE POWER SUPPLY
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FIG. 2

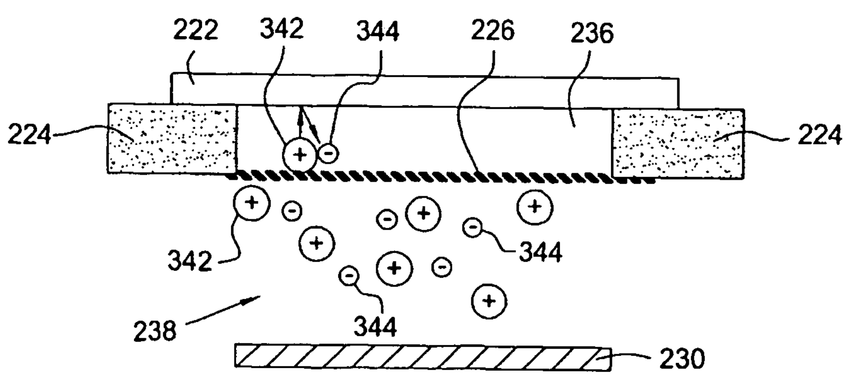
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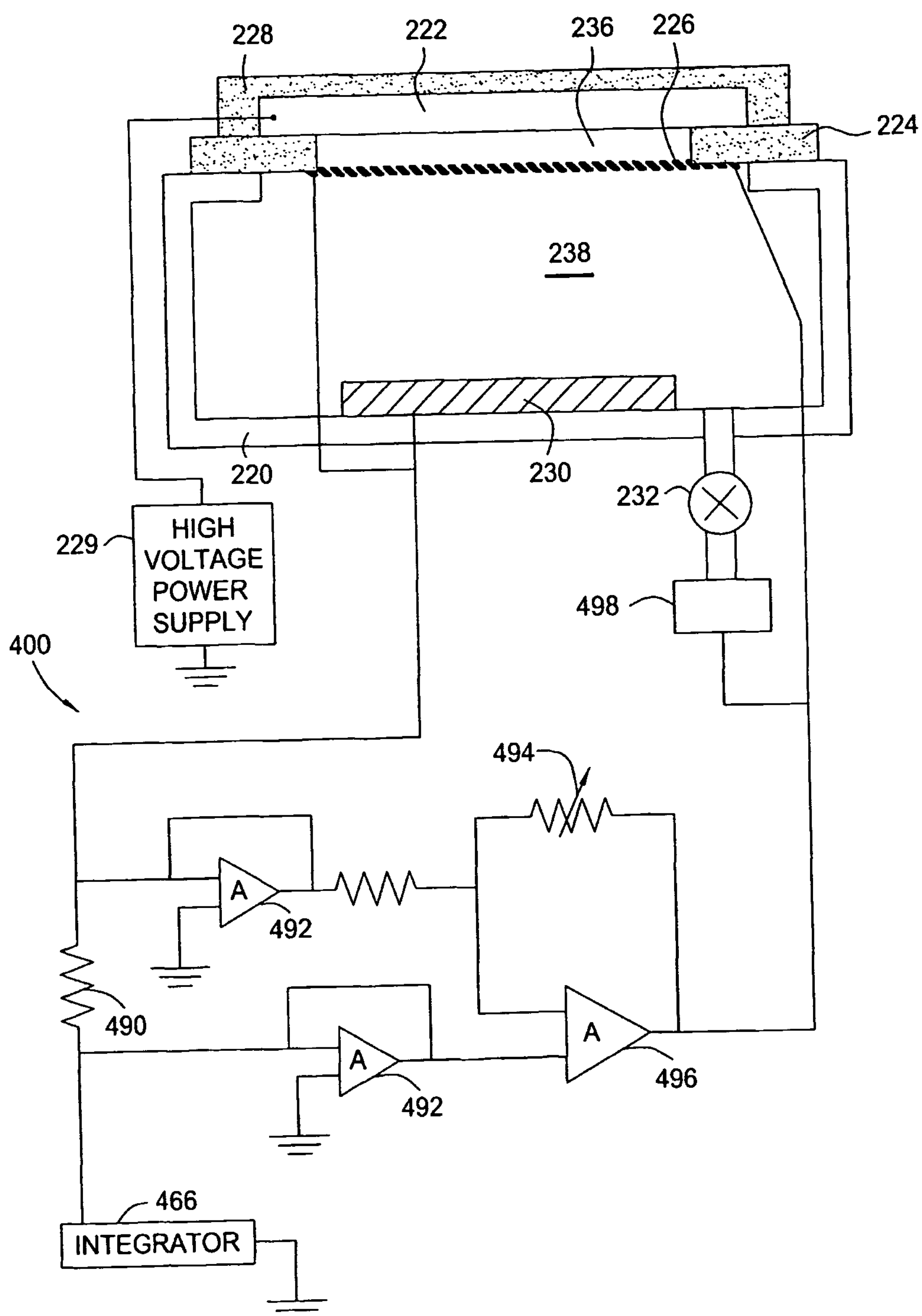
FIG. 3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HIGH VOLTAGE POWER SUPPLY
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490
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A
496
466
INTEGRATOR

FIG. 4